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(54) Process for preparing propylene copolymers

(57) Described herein is a process for preparing propylene copolymers. The process comprises the steps of polymerizing propylene with comonomers in at least one slurry reactor and at least one gas phase reactor, at least 10 % of the polymer product being produced in the gas phase reactor(s); recovering from the slurry reactor a copolymerization product containing unreacted monomers and conducting the copolymerization product to a first gas phase reactor essentially without recycling of the unreacted monomers to the slurry reactor before the gas phase reactor. The process will provide high randomness copolymers, which are very soft.

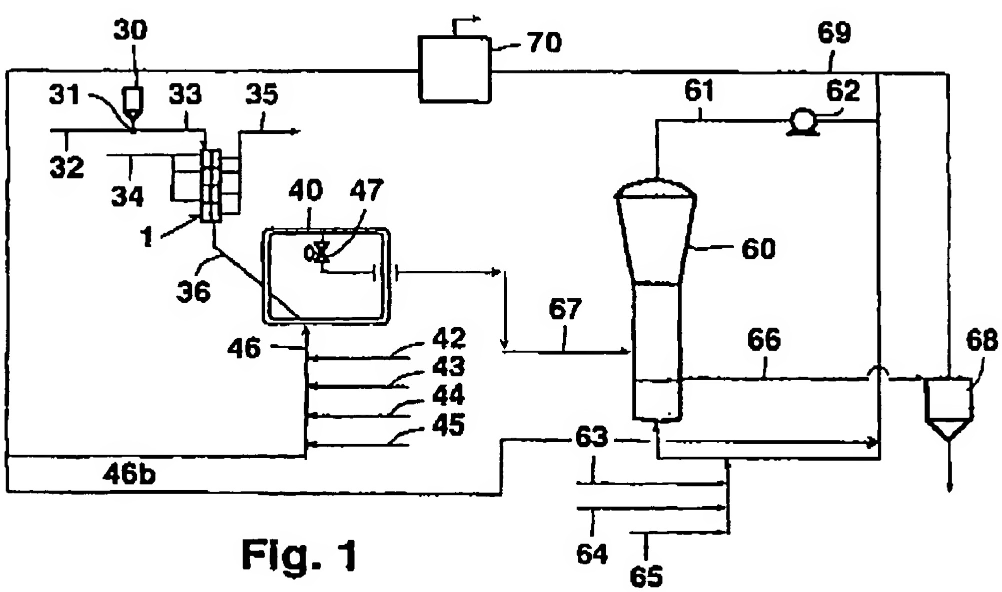

Fig. 1

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Description

Background of the Invention

Field of the Invention

The present invention relates to the production of propylene based copolymers having a high comonomer content. In particular, the present invention concerns a process for preparing propylene copolymers in a reactor system comprising a combination of at least one slurry reactor and at least one gas phase reactor. The invention also concerns an apparatus for carrying out the process.

Description of Related Art

The softness, impact resistance and heat sealing properties of propylene-based polymers can be increased by copolymerizing propylene with other olefins, such as ethylene, i-butylene and the like. Both bulk and gas phase processes have been employed. However, the comonomers used during polymerization cause swelling of the polymers in the polymerization medium of bulk processes. As a result, when swollen and soft polymer particles are flashed after polymerization, the morphology of the particles is destroyed and the bulk density of the powderized polymer becomes very low. At the same time amorphous material accumulates on the surfaces of the powder. Sticky low-density material agglomerates easily on the walls in the flash tank and causes problems during transportation. These problems increase when the proportion of comonomers increases

For this reason, in the prior art the polymerization has mainly been carried out by using gas phase processes. These processes have thus been proposed for the production of sticky, but fluidizable products (EP 0 237 003) and for rubbery products, e.g. EPR and EPDM, (EP 0 614 917). In said processes, the gas velocity of the fluidized bed reactor is sufficient to cause the particles to separate and act as a fluid. However, the polymer in the fluid bed reactor is passed through essentially in a plug flow mode.

Gas phase processes are also favoured for high comonomer content products. cf. EP 0 674 991, EP 0 584 574, EP 0 605 001 and EP 0 704 464.

However, a problem relating to gas phase reactors is formed by their long residence times which means long transition times and possible productions losses. This is especially true for multireactor processes. Catalyst productivity in a gas phase process is low, which means higher catalyst and production costs.

In order to draw benefits from the different advantages of the slurry bulk and the gas phase reactors, respectively, some combinations of bulk and gas phase reactors for preparing copolymers of propylene have been suggested in the art. However, to date, none of the prior art processes meets the requirements for flexibility and low production costs dictated by the production of large varieties of polyolefin qualities using one and the same process configuration. In particular. recycling of rather large amounts of unreacted monomers to the slurry reactor, which is a typical feature of the known processes, impairs the loop reactor dynamics and slows up the transition to novel product qualities.

An improved two-stage process for polymerization of propylene in a combination of a loop reactor and a gas phase reactor is disclosed in US Patent No. 4,740,550. The main object of US 4.740.550 is to provide a process for preparing a block copolymer of high quality by feeding homopolymer with narrow residence time distribution to the block copolymerization stage. The process disclosed comprises the following stages: a first stage consisting of homopolymerization in a bulk loop reactor, a second stage homopolymenzation in a gas phase reactor, fines removal in a cyclone between the first and second stage, and, finally, impact copolymerization in an additional gas phase reactor.

Before the polymerization product of the loop reactor is fed into the gas phase the fines fraction is removed and circulated back to the loop reactor. Together with the fines a part of the monomers from the gas phase reactor is recycled directly to the first stage loop reactor.

There are some considerable problems related to this prior art. Thus. If all fines are removed from the reactor outlet of the loop reactor and circulated back to the loop reactor, there is a considerable risk that the loop reactor eventually will be filled with inactive catalyst or slightly polymerized dead fines. On the other hand, if a portion of the fines stream would be combined with the product from the last reactor this might cause inhomogenity problems in the final product. Further, if a portion of the fines stream is separately collected and blended with a separate homopolymer as also suggested in US 4,740,550. this leads to complicated and economically unacceptable operation.

Summary of the Invention

It is an object of the present invention to eliminate the problems related to the prior art of single and multiple-reactor processes and to provide a novel process for preparing copolymers of propylene.

It is another object of the invention to provide a highly versitile process which can be used for preparing a wide range of different copolymer products of propylene.

It is a third object of the invention to provide an apparatus for producing propylene copolymers.

These and other objects, together with the advantages thereof over known processes, which shall become apparent from specification which follows. are accomplished by the invention as hereinafter described and claimed

The process according to the present invention is

based on a combination of at least one slurry reactor and at least one gas phase reactor connected in series, in that order, to form a cascade. Propylene copolymers are prepared in the presence of a catalyst at elevated temperature and pressure. According to the invention, the polymerization product of at least one slurry reactor, containing unreacted monomers, is conducted to the first gas phase reactor with minimum or no recycling of monomer back to the slurry reactor. In connection with the present invention it has been found that impact copolymers of high quality can be produced with a two-stage homopolymerization followed by a impact copolymerization step without any fines removal and circulation either after the first or second stage copolymerization. In the present invention, it is possible to minimize the amount of circulation by using the specific sequence of reactors and by selecting the relative amounts produced in each reactor with that object in mind.

According to another aspect of the invention, at least one slurry reactor and at least one gas phase reactor connected in series are employed as a reactor system, the at least one slurry reactor being a bulk loop reactor operated at high or super critical temperature, and the content of the slurry reactor, including the copolymer product and reaction medium containing unreacted monomers, is led directly into the gas phase reactor fluidized bed using a conduit interconnecting the slurry reactor and the gas phase reactor.

More specifically, the process according to the present invention is mainly characterized by what is stated in the characterizing part of claim 1.

The apparatus according to the present invention is characterized by what is stated in the characterizing part of claim 32.

The invention achieves a number of considerable advantages. With the present arrangement it has been found that the monomers fed into the first reactor can, to a large extent or fully, be consumed in the gas phase reactor(s) after the slurry reactor. This is possible due to gas phase operation with small amount of gas leaving with the polymer product. The loop reactor dynamics in the cascade provides fast transitions and high productivity. Fast start-ups are also possible because the gas phase bed material is available directly from the loop reactor. With the loop and gas phase reactor cascade it is possible to produce a large variety of different broad molecular weight distribution or bimodal products. The at least one gas phase reactor provides high flexibility in the reaction rate ratio between the first and second part of the product because of adjustable bed level and reaction rate. Further, the gas phase reactor having no solubility limitations makes it pssible to produce polymers of high and very high comonomor content.

The loop-gas phase reactor combination have greatly reduced residence times and production losses in comparison to gas phase - gas phase multireactor processes.

Brief Description of the Drawings

Figure 1 depicts in a schematic fashion the process configuration of a first preferred embodiment of the invention; and

Figure 2 depicts in a schematic fashion the process configuration of a second preferred embodiment of the invention.

Detailed Description of the Invention

Definitions

For the purpose of the present invention, "slurry reactor" designates any reactor, such as a continuous or simple stirred tank reactor or loop reactor, operating in bulk or slurry and in which the polymer forms in particulate form. "Bulk" means a polymerization in reaction medium that comprises at least 60 wt-% monomer. According to a preferred embodiment the slurry reactor comprises a bulk loop reactor.

By "gas phase reactor" is meant any mechanically mixed or fluid bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec.

"High temperature polymerization" stands for polymerization temperatures above a limiting temperature of 80 °C known to be harmful for high yield catalysts of related prior art. At high temperatures the stereospecificity of the catalyst and the morphology of the polymer powder can be lost. This does not take place with the particularly preferred type of catalysts used in the invention which is described below. The high temperature polymerization takes place above the limiting temperature and below the corresponding critical temperature of the reaction medium.

"Super critical polymerization" designates polymerization that takes place above a corresponding critical temperature and pressure of the reaction medium.

By "direct feed" is meant a process in which the content of a slurry reactor, comprising the polymerization product and the reaction medium, is lead directly to the fluidized bed of a gas phase reactor.

"Reaction zone " stands for one or several reactors of similar type producing the same type or characteristics of polymer connected in the series.

The expressions "essentially without monomer recycling" and "with minimum or no monomer recycling" are synonymously used to indicate that no more than about 30 wt-%, preferably less than 20 wt-% and in particular none of the monomers is recycled to the slurry reactor. By contrast, in a normal slurry process, 50 wt-% or more of the monomer is recycled.

The overall process

The present invention concerns a multistage process consisting of a bulk reaction zone including at least

one slurry reactor, and a gas phase reaction zone including at least one gas phase reactor in cascade after at least one slurry reactor with a minimum or no recycling of monomer back to the first reactor and with direct feed or indirect feed to the gas phase for homo- or copolymerizing propylene.

In the direct feed process the content of the slurry reactor, the polymerization product and reaction medium, is conducted directly to the fluidized bed reactor. The product outlet from the slurry reactor can be discontinuous, or preferably continuous. The slurry is led as such without separation of any gases or particle streams based on different particle size. No particles are recycled to the preceding reactor. Optionally, the line between the slurry reactor and the gas phase reactor can be heated in order to evaporate only a part or all of the reaction medium before it enters the gas phase reactor polymer bed.

The reaction is continued in the gas phase reactor(s). All or practically all (at least about 90 %) of the monomer entering the gas phase from the slurry reactor is part of the reactor gas inventory until it is converted into the polymer.

In two reactor operation the polymer leaving the gas phase reactor with the outlet system enters a solid/gas separation unit. The polymer from the bottom is fed to further processing steps and the gas is compressed and circulated back to the gas phase reactor after purification steps. Typically light inerts, such as methane and ethane, and heavier inerts such as propane and oligomers are removed in these purification steps. The purification can be performed with distillation or membrane separation. In case of distillation the monomers are circulated back to the gas phase reactor mainly as liquid.

In three reactor operation the polymer leaving the 1st gas phase reactor with the outlet system enters a solid/gas separation unit. The polymer from the bottom is fed further to 2nd gas phase reactor and the gas is compressed and circulated back to the 1st gas phase reactor after purification steps. Typically light inerts, such as methane and ethane, and heavier inerts such as propane and oligomers are removed in these purification steps. The purification can be performed with distillation or membrane separation. In case of distillation the monomers are circulated back to the gas phase reactor mainly as liquid.

Optionally in three reactor operation the polymer leaving the 1st gas phase reactor with the outlet system enters the 2nd gas phase reactor directly with the accompanying gas.

In three reactor operation the polymer leaving the 2nd gas phase reactor with the outlet system enters a solid/gas separation unit. The polymer from the bottom is fed to further processing steps and the gas is compressed and partly circulated back to the 2nd gas phase reactor directly, partly after purification steps. Typically light inerts, such as methane and ethane, and heavier inerts such as propane and oligomers are removed in these purification steps. The purification can be performed with distillation or membrane separation. In case of distillation an ethylene rich stream is circulated back to the 2nd gas phase reactor and a propylene-propane stream is fed to propane and oligomers removal steps.

The polymerization products are obtained by using a catalyst. The catalyst can be any catalyst providing adequate activity at elevated temperature. The preferred catalyst system used comprises a high yield Ziegler-Natta catalyst having catalyst component, a co-catalyst component, an external donor and, optionally, an internal donor. Another preferred catalyst system is a metallocene-based catalyst, e.g. having a bridged ligand structure giving high stereoselectivity, and which is impregnated on a carrier or support in the form of an activated complex.

The polymerization temperature is 60 to 85 °C. The slurry reactor is operated at elevated pressure at least 35 bar up to 100 bar, and the gas phase reactor(s) at least 10 bar up to dew point pressure. Alternatively any reactor of the reactors in the series can be operated above the critical temperature and pressure.

Propylene and one or more other C_2 to C_{16} olefins, e.g. ethylene, 1-butene, 4-methyl-1-pentene, 3-methyl-1-butene, 1-hexene, 1-octene, 1-decene, dienes, or cyclic olefins, e.g. vinylcyclohexane or cyclopentene, is subjected to polymerization and copolymerization, respectively, in a plurality of polymerization reactors connected in series. The comonomer olefin(s) can be used in any of the reactors. Different amounts of hydrogen can be used as a molar mass modifier or regulator in any or every reactor.

The desired copolymers of propylene can be recovered from the product separation means of the gas phase reaction zone.

The catalyst

The polymerization products are obtained by using a catalyst. As catalyst any stereospecific catalyst for propylene can be used, which has high yield and useful polymer properties e.g. isotacticity and morphology at the high temperature and possible supercritical polymerization. The preferred catalyst system used comprises a high yield Ziegler-Natta catalyst having catalyst component, a cocatalyst component, optionally, an external donor and an internal donor. Another preferred catalyst system is a metallocene catalyst having a bridged ligand structure giving high stereoselectivity, and which has an active complex impregnated on a carrier. Finally, the catalyst is preferably any other catalyst providing adequate activity at elevated temperature.

Examples of suitable systems are described in, for example, FI Patents Nos. 86866, 96615 and 88047, 88048 and 88049.

One particularly preferable catalyst, which can be used in the present invention is disclosed in FI Patent No. 88047. Another preferred catalyst is disclosed in FI

Patent Application No. 963707.

Further preferred catalysts are disclosed in PCT/FI 97/00191 and PCT/FI97/00192.

Prepolymerization

The catalyst can be prepolymerized prior to feeding into the first polymerization reactor of the series. During prepolymerization the catalyst components are contacted with a monomer, such as an olefin monomer, before feeding into the reactor. Examples of suitable systems are described in, for example, FI Patent Application No. FI 961152.

It is also possible to carry out the prepolymerization in the presence of a viscous substance, such as an olefinic wax, to provide a prepolymerized catalyst which is stabile during storage and handling. The catalyst prepolymerized in wax will allow for easy dosing of the catalyst into the polymerization reactors. Examples of suitable systems are described in, for example, FI Patent No. 95387. Typically about 1 part of catalyst is used for a maximum of 4 parts of polymer.

The monomer used for prepolymerization can be selected from the group consisting of propylene, 1-butene, 4-methyl-1-pentene, 3-methyl-1-butene, vinylcyclohexane, cyclopentene, 1-hexene, 1-octene, and 1-decene.

The prepolymerization can be performed batchwise in wax or in a continuous prepolymerization reactor or in a continuous plug flow type prepolymerization reactor.

Polymerization

The invention is based on the combination of at least one slurry reactor and at least one gas phase reactor connected in series, called a cascade.

The equipment of the polymerization step can comprise polymerization reactors of any suitable type. The slurry reactor can be any continuous or simple stirred tank reactor or loop reactor operating in bulk or slurry and the polymer forms in particular form in the reactor. Bulk means a polymerization in reaction medium that comprises of at least 60 % (w/w) monomer. The gas phase reactor can be any mechanically mixed or fluid bed reactor. According to the present invention the slurry reactor is preferably a bulk loop reactor and the gas phase reactor is a fluidized bed type reactor with a mechanical stirrer.

Any reactor in the process can be a super critical polymerization reactor.

The production split between the slurry reactor and the 1st gas phase reactor(s) is 65:35-50:50 when monomer recycling back to the slurry reactor is allowed. In contrast, the production split between the slurry reactor and the gas phase reactor(s) is less than or equal to 50:50 when no recycling back to the slurry reactor is required. In all the cases the production split is more than 10:90. Thus, according to a preferred embodiment, 10 to 50 wt-% of the polymer is prepared in the slurry reaction zone and no monomer is recycled to the slurry reactor zone. When 50 % to 65 % of the polymer is prepared in the slurry reaction zone, a small monomer amount of the monomer has to be recycled to the slurry reactor from the gas phase reaction zone.

According to the invention, the polymerization process comprises at least the following steps of

- subjecting propylene and optionally other olefins to polymerization or copolymerization in a first slurry polymerization zone or reactor,
- recovering the first polymerization product from the first reaction zone with the reaction medium,
- directly or indirecly feeding the first polymerization product into a gas phase polymerization zone or reactor,
- optionally feeding additional propylene and/or comonomer(s) to the second reaction zone,
- subjecting the excess propylene and/or comonomers from 1st zone and additional propylene and/or comonomer(s) to a second polymerization reaction in the presence of the first polymerization product to produce a second polymerization product,
- recovering the polymerization product from second reaction zone, and
- separating and recovering the polypropylene from the second reaction product.

Additionally the process can also comprise one or more of the following additional steps

- prepolymerizing catalyst with one or more monomer(s),
- separating gas from the second reaction zone product,
- feeding the recovered polymerization product of the earlier zones to a third or fourth reaction zone or reactor,
- optionally feeding additional propylene and/or comonomer(s) to the third and fourth reaction zone,
- subjecting the excess propylene and/or comonomer(s) and additional propylene and/or comonomers to third and fourth polymerization reaction in the presence of the polymerization product of the earlier zones to produce a third or fourth polymerization product, and
- recovering the polymerization product from the third or fourth reaction zone, and
- separating and recovering the polypropylene from the third or fourth reaction product.

In the first step of the process, propylene with the optional comonomer(s) together with the activated catalyst complex and optional cocatalyst and other aid components are fed into the first polymerization reactor. The catalyst can be prepolymerized or it is prepolymerized before feeding to the process. Along with the afore-

mentioned components hydrogen as a molar mass regulator can be fed into the reactor in the amount required for achieving the desired molar mass of the polymer. In the embodiment of no circulation back to the slurry reactor only fresh monomer is fed into the first reactor.

Alternatively, in the embodiment of minimum recycling of the monomer back to the slurry reactor. the feed of the reactor can consist of the recycled monomer from the following reactor(s), passed through a recovery system, if any, together with added fresh monomer, hydrogen, optional comonomer(s) and catalyst components.

In all of the embodiments the presence of propylene, optional comonomer(s), cocatalyst and other aid components, the activated catalyst complex will polymerize and form a product in particulate form, i.e. polymer particles, which are suspended in the fluid circulated in the reactor.

The polymerization medium typically comprises the monomer and optionally a hydrocarbon. and the fluid is either liquid or gaseous. In the case of slurry reactor, in particular a loop reactor, the fluid is liquid and the suspension of polymer is circulated continuously through the slurry reactor, whereby more suspension of polymer in particle form in hydrocarbon medium or monomer will be produced. According to preferred embodiment, the first polymerization or copolymerization reaction is carried out in a reaction medium mainly consisting propylene. Preferably at least 60 weight percent of the medium is propylene.

The conditions of the slurry reactor are selected so that at least 10 wt-%, preferably at least 12 wt-% of the whole production is polymerised in the first slurry reactor. The temperature is in range of 60 to 85 °C, and even more preferably for homopolymers and high randomness copolymer 75 to 85 °C and for copolymers of high comonomer content 60 to 75 °C. The reaction pressure is in the range of 30 to 100 bar, preferably 35 to 80 bar.

In slurry polymerization zone more than one reactor can be used in series. In such a case the polymer suspension in an inert hydrocarbon or in monomer produced in the 1st slurry reactor is fed without separation of inert components and monomers periodically or continuously to the following slurry reactor. which acts at lower pressure than the previous slurry reactor.

The polymerization heat is removed by cooling the reactor with a cooling jacket. The residence time in the slurry reactor must be at lest 10 minutes, preferably 20-100 min for obtaining a sufficient degree of polymerization. This is necessary to achieve polymer yields of at least 40 kg PP/g cat. It is also advantageous to operate the slurry reactor with high solid concentrations, e. g. 50 % for homopolymers and 35 or 40 % for some copolymers when the particles are swelling. If the solid concentration in the loop reactor is too low, the amount of reaction medium conducted to the second reaction zone or gas phase reactor is increasing.

The content of the slurry reactor, the polymerization product and reaction medium, is led directly to the next gas phase reactor fluidized bed.

The second reactor is preferably a gas phase reactor, wherein propylene and optionally comonomer(s) are polymerized in reaction medium which consists of gas or vapour.

The gas phase reactor can be an ordinary fluidized bed reactor, although other types of gas phase reactors can be used. In a fluidized bed reactor, the bed consists of the formed and growing polymer particles as well as still active catalyst come along with the polymer fraction. The bed is kept in a fluidized state by introducing gaseous components, e.g. monomer on such flow rate (at least 0.2 m/s) which make the particles act as a fluid. The fluidizing gas can contain also inert gases, like nitrogen and also hydrogen as a modifier. In the invention it is not recommendable to use unnecessary inert gases, which may cause problems in the recovery section.

The gas phase reactor used can be operated in the temperature range of 50 to 115 °C, preferably between 60 and 110 °C and reaction pressure between 10 and 40 bar and the partial pressure of the monomer is preferably between 2 and 30 bar or more, but always below the dew point pressure.

According to one preferred embodiment, no fresh propylene is fed to the first gas phase reactor other than what is required for various flushings.

The pressure of the second polymerization product including the gaseous reaction medium is then reduced after the first gas phase reactor in order to separate part of the gaseous and possible volatile components (e.g. heavy comonomers and compounds used for catalyst feeds) of the product e.g. in a flash tank. The overhead gas stream is recirculated through the recovery system back to the first gas phase reactor or partly to the first gas phase reactor and partly to the slurry reactor. Some of the monomers, typically the heavier comonomers, can be recycled to the bulk reaction zone.

If desired, the polymerization product can be fed into a second gas phase reactor and subjected to a third polymerization reaction to produce a modified polymerization product from which the polypropylene is separated and recovered. The third polymerization reaction is carried out in a gas phase reactor in the presence of comonomers which give the third polymerization product properties, e.g. softness.

Summarising what has been stated above, one particularly preferred embodiment of the invention comprises (Fig. 1)

- polymerizing propylene in a loop reactor at a pressure of 40 to 80 bar, at a temperature of 80 to 100 °C and hydrogen is used to control the molar mass of the polymerization product,
- recovering the polymerization product from the loop reactor and conducting it to a gas phase reactor fluid bed,
- optionally feeding additional propylene and optional comonomer to the gas phase reactor,

- optionally feeding additional hydrogen to the gas phase reactor to control the hydrogen-to-propylene ratio to provide the desired molecular mass of the polymerization product,
- recovering the polymerization product from the gas phase reactor and conducting it to a flash tank, wherein the pressure of the product is reduced to produce an overhead product containing essentially non-reacted propylene and hydrogen and a bottom product primarily containing polymerized solids,
- recycling the overhead product or at least a major part of it to the gas phase reactor via a recovery section, and
- recovering polypropylene polymer as the bottom product of the flash tank.

According to the second particularly preferred embodiment (Fig. 1):

- propylene and copolymer(s), e.g. ethylene or 1-butene or both, are polymerised in a loop reactor at a pressure of 40 to 80 bar, at a temperature of 60 to 80 °C and hydrogen is used to provide a polymerization product having the desired molar mass,
- the polymerization product from the loop reactor is conducted directly to a gas phase reactor fluid bed,
- optionally additional propylene and comomomer(s) are fed to the gas phase reactor,
- optionally additional hydrogen is fed to the gas phase reactor to control the hydrogen-to-propylene ratio to provide desired molecular mass of the polymerization product,
- the polymerization product is recovered from the gas phase reactor and conducted to a flash tank, wherein the pressure is reduced to produce an overhead product containing essentially non-reacted monomers and hydrogen and a bottom product primarily containing polymerized solids,
- the overhead product or at least a major part of it is recycled to the gas phase reactor via a recovery section, and
- polypropylene polymer is recovered as the bottom product of the flash tank.

According to the third particularly preferred embodiment (Fig. 2):

- propylene and optionally comonomers are polymerised in a loop reactor at a pressure of 40 to 80 bar, at a temperature of 60 to 100 °C and hydrogen is used to control the molar mass of the polymerization product,
- the polymerization product from the loop reactor is recovered and conducted to a gas phase reactor fluid bed,
- optionally additional propylene and optional comonomer is fed to the gas phase reactor,
- additional hydrogen is optionally fed to the gas phase reactor to control the hydrogen-to-propylene ratio to provide desired molecular mass of the polymerization product,
- the polymerization product from the first gas phase reactor is recovered and conducted to an intermediate flash tank, wherein the pressure of the product is reduced to produce an overhead product containing essentially non-reacted monomer(s) and hydrogen and a bottom product primarily containing polymerised solids,
- the overhead product or at least a major part of it is recycled to the first gas phase reactor via a recovery section,
- the polypropylene polymer from the bottom of the intermediate flash tank is fed to a third polymerization reaction via a polymer feed system,
- the third polymerization reaction is carried out in a gas phase reactor in the presence of comonomers,
- the polymerization product from the second gas phase reactor is recovered and conducted to a flash tank, wherein the pressure of the product is reduced to produce an overhead product containing essentially non-reacted monomer(s) and hydrogen and a bottom product containing primarily polymerised solids,
- optionally the polymerization product from the third polymerization can be conducted directly or via a flash tank to a third (fourth etc.) gas phase polymerization reactor, wherein polymerization is carried out in the presence of comonomers.

These above-mentioned two preferred embodiments are also depicted in the attached drawings, which illustrate the particular configuration of process equipment used. The numerals refer to the following pieces of equipment:

1; 101	prepolymerization reactor
30; 130	catalyst reservoir
31; 131	feeding device
32; 132	diluent (optional)
33; 133	catalyst/diluent mixture
34; 134	monomer
35; 135	cocatalyst and possible donors
40; 140	loop reactor
42; 142	diluent feed (optional)
43; 143	monomer feed
44; 144	hydrogen feed
45; 145	comonomer feed (optional)
46; 146	back to the loop reactor 40; 140 through the line 46; 146
47; 147	one or several exhaust valve
150b	flash separator
152b	removing line
60; 160; 160b	gas phase reactor
61; 161; 161b	gas transfer line
62; 162; 162b	compressor

63; 163; 163b	monomer feed
64; 164; 164b	comonomer feed
65; 165; 165b	hydrogen feed
66; 166; 166b	transfer line
67; 167	product transfer line
68; 168	polymer product recovery system, e. g. flash tank
69; 169	recovery line
70; 170	monomer recovery system

Turning to figure 1, it can be noted that catalyst from reservoir 30 is fed to the feeding device 31 together with optional diluent from line 32. The feeding device 31 feeds the catalyst/diluent mixture into the prepolymerization chamber 1 via line 33. Monomer is fed through 34 and cocatalyst and possible donors can be fed into the reactor 1 through conduits 35 or, preferably, the cocatalyst and donor(s) are intermixed and fed in line 35.

From the prepolymerization chamber 1 the prepolymerized catalyst is removed preferably directly through line 36 and transferred to a loop reactor 40. In the loop reactor 40 the polymerization is continued by adding an optional diluent from the line 42, monomer from line 43, hydrogen from line 44 and an optional comonomer from line 45 through the line 46. An optional cocatalyst can also be introduced into the loop reactor 40.

From the loop reactor 40 the polymer-hydrocarbon mixture is fed through one or several exhaust valves 47 described in, e.g., FI Patent Applications Nos. 971368 or 971367. There is a direct product transfer 67 from the loop reactor 40 to gas phase reactor 60.

In the lower part of the gas phase reactor 60 there is a fluid bed consisting of polymer particles, which will be kept in a fluidized state in an ordinary way by circulating the gases removed from the top of the reactor 60 though line 61, compressor 62 and a heat exchanger (not presented) to the lower part of the reactor 60 in an ordinary way. The reactor 60 is advantageously, but not necessarily, equipped with a mixer (described in FI Patent Application No. 933073, not shown in the figure). To the lower part of the reactor 60 can be led in a well known way monomers from line 63, optionally comonomer from line 64 and hydrogen from the line 65. The product will be removed from the reactor 60 continually or periodically through the transfer line 66 to the flash tank 68. The overhead product of the recovery system is circulated to the gas phase reactor via a monomer recovery system.

The embodiment shown in Figure 2 differs from the one in Figure 1 only in the sense that product from gas phase reactor 160 is fed into the additional gas phase reactor 160b. The polymer particles are removed from the flash tank 168 and the polymer feed tank 150b through the removing line 152b to the gas phase reactor 160b. The gas phase reactor is advantageously equipped with a mixer (not shown).

The overhead of the flash separator 168b is recycled partly to the gas phase reactor 160b and partly to the monomer recovery system.

In both of the above presented embodiments, the numerals 70 and 170 signify separation means, such as membrane unit or stripping columns, which are capable of freeing the recycle monomer of the gas phase reactor(s) (60, 160 and 160b) or of the separators (68, 168 and 168b) from hydrogen and/or light inert hydrocarbons typically having a lower boiling point than the monomer(s).

The polymers

The products produced according to the present invention are polypropylene copolymers including polypropylene terpolymers. In particular, it is possible by means of the present invention to produce high randomness copolymers, which are very soft. The copolymers contain at least 0.5 wt-% of a comonomer, in particular at least about 2 wt-% and preferably up to 20 wt-% of a comonomer. A typical comonomer content is about 2 to 12 wt-%. An essential feature of the invention is the high polymerization temperature used, preferably above 75 °C, which will provide a more even comonomer distribution during copolymerizations. The randomness, measured by FTIR, at a polymerization temperature of 60 °C is 69 %, at 65 °C 71 %, and at a polymerization temperature of 75 °C in the first reactor and 80 °C in the second reactor 74 %.

The following non-limiting examples illustrate the principles of the present invention.

Example 1

A production scale plant was simulated to produce continuously random PP polymer. The plant comprises catalyst, alkyl, donor, propylene and ethylene feed systems, a prepolymerization reactor, a loop reactor and a fluidized bed gas phase reactor (GPR).

Catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to a loop reactor to which also ethylene, hydrogen and more propylene was fed. The polymer slurry from the loop reactor and additional hydrogen, ethylene and propylene were fed to the GPR. The production in the reactors were 300 kg/h in prepolymerization, 15 t/h in loop and 10 t/h in GPR.

The prepolymerization reactor was operated at a pressure of 56 bar and a temperature of 20 °C. The loop reactor was operated at a 55 bar pressure and a 75 °C temperature. The MFR (2.16 kg, 230 °C) of the random-PP produced in the loop was set at 7 by adjusting the hydrogen feed and the ethylene content was set at 3.5 % w/w via ethylene feed.

The GPR was operated at pressure of 35 bar and a temperature of 80 °C. The MFR (2.16 kg, 230 °C) of the random-PP in taken out of the GPR was adjusted to 7 via the partial pressure of hydrogen and ethylene content was adjusted to 3.5 % w/w via the partial pressure

of ethylene. 5 t/h of propene and 33 kg/h ethylene were recirculated from the GPR outlet back to the loop reactor. The once-through conversions of propylene and ethylene were 83 % and 96 %, respectively.

Example 2

A pilot plant operated continuously is used to produce PP-copolymer with good impact and creep properties. The plant comprises a catalyst, alkyl, donor, propylene and ethylene feed systems, a prepolymerization reactor, a loop reactor and 2 fluidized bed gas phase reactors (GPR).

Catalyst, alkyl, donor and propylene are fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor is fed to a loop reactor into which also hydrogen, ethylene and additional propylene are fed.

The polymer slurry from the loop reactor and additional hydrogen and propylene are fed to the 1st GPR. The polymer from 1st GPR is fed to 2nd GPR. Ethylene, some hydrogen and additional propylene was fed to the second GPR. The formed polymer and unreacted propylene are separated after removal from the 2nd GPR.

The catalyst used is a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst is contacted with triethylaluminium (TEA) and dicyclopentyldimethoxysilane (DCP-DMS) (Al/Ti ratio is 150 and Al/Do 10 (mole)) before feeding to the prepolymerization reactor.

The catalyst is fed according to U.S. Patent No. 5,385.992 and is flushed with propylene to the loop reactor. The prepolymerization reactor is operated at a pressure of 51 bar and a temperature of 20 °C and a mean residence time of the catalyst amounting to 7 min.

The loop reactor is operated at a 50 bar pressure, 75 °C temperature and mean residence time of the catalyst at 1 h. The MFR (2.16 kg, 230 °C) of the PP-random polymer produced in the loop is controlled to be 7 via hydrogen feed. The ethylene content is controlled to be 3.5 % w/w via ethylene feed.

The polymer slurry from the loop reactor is transferred to the 1st GPR. The 1st GPR reactor is operated at 29 bar total pressure and 21 bar partial pressure of propylene, 80 °C temperature and mean residence time of the catalyst at 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer taken out of the GPR is controlled to be 10 via partial pressure of hydrogen. The ethylene content is controlled to be 2 % w/w via production split between the reactors.

The polymer from the 1st GPR is transferred to the 2nd GPR. The 2nd GPR reactor is operated at a total pressure of 10 bar and a partial monomer pressure of 7 bar, a temperature of 80 °C and a mean residence time of the catalyst of 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-copolymer taken out of the GPR is adjusted to 7 using partial pressure of hydrogen. The ethylene content is adjusted to 10 % w/w via partial pressure of ethylene and controlling the production split between the reactors.

The desired properties are achieved with a production split comprising 1 % in prepolymerization, 40 % in loop and 40 % in the first GPR and 19 % in the second GPR.

Example 3

A pilot plant operated continuously was used to produce very soft PP-copolymer. The plant comprises a catalyst, alkyl, donor, propylene and ethylene feed systems, prepolymerization reactor, loop reactor and a fluidized bed gas phase reactor (GPR).

Catalyst, alkyl, donor and propylene was fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to a loop reactor in which also hydrogen, ethylene and additional propylene was fed.

The polymer slurry from the loop reactor and additional ethylene, hydrogen and propylene were fed to the GPR. The formed polymer and unreacted monomers were separated after removal from GPR.

The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent 5.234.879. The catalyst was contacted with triethylaluminium (TEA) and dicyclopentyldimethoxysilane (DCP-DMS) (Al/Ti ratio was 150 and Al/Do 10 (mole)) before feeding to the prepolymerization reactor.

The catalyst was fed according to U.S. Patent US-5.385.992 and was flushed with propylene to the loop reactor. The prepolymerization reactor was operated at 51 bar pressure, 20 °C temperature and mean residence time of the catalyst at 7 min.

The loop reactor was operated at 50 bar pressure, 75 °C temperature and mean residence time of the catalyst at 1 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer produced in the loop was controlled to be 4 via hydrogen feed. The ethylene content was controlled to be 3.8 % w/w via ethylene feed.

The polymer slurry from the loop reactor was transferred to the 1st GPR. The 1st GPR reactor was operated at 29 bar total pressure and 21 bar partial pressure of propylene, 80 °C temperature and mean residence time of the catalyst at 1.2 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer taken out of the GPR was controlled to be 2.5 via partial pressure of hydrogen. The ethylene content was controlled to be 8 % w/w via production split between the reactors and partial pressure of ethylene.

Desired properties are achieved with a production split of 1 % in prepolymerization, 45 % in loop and 55 % in the GPR.

The polymer from the GPR could have been transferred to another GPR to produce even softer PP copolymer by having even higher partial pressure of ethylene in the 2nd GPR.

Example 4

A pilot plant operated continuously was used to produce PP-randompolymer. The plant comprises a catalyst, alkyl, donor, propylene and ethylene feed systems, loop reactor and a fluidized bed gas phase reactor (GPR). Said components are fed to the loop reactor. The polymer slurry from the loop reactor and additional hydrogen, propylene and ethylene was fed to GPR. The formed polymer and unreacted propylene where separated after removal from GPR.

The catalyst used was a highly active and stereospecific ZN-catalyst made according to U S. Patent No. 5,234,879. The catalyst was prepolymerized with propylene (the mass ratio of PP/cat was 10) in batch according to Finnish Patent No. 95387. The prepolymerized catalyst was contacted with triethylaluminium (TEA) and dicyclopentyldimethoxysilane (DCPDMS) (Al/Ti ratio was 140 and Al/Do 10 (mole)) before feeding to the loop reactor.

The catalyst was fed according to US Patent 5,385,992 and was flushed with propylene to the loop reactor. The loop reactor was operated at 50 bar pressure, 75 °C temperature and mean residence time of the catalyst at 1 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer produced in the loop was controlled to be 4 via hydrogen feed. The ethylene content was controlled to be 3.5 % w/w via ethylene feed.

The polymer slurry from the loop reactor was transferred to the GPR. The GPR reactor was operated at a total pressure of 29 bar and a partial pressure of propylene of 21 bar, a temperature of 80 °C, and a mean residence time of the catalyst of 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-random polymer taken out of the GPR was adjusted to 4 by controlling the partial pressure of the hydrogen. The ethylene content was controlled to be 3.5 % w/w via partial pressure of ethylene. Production split between the reactors was 55 % in loop and 45 % in GPR.

Example 5

A pilot plant operated continuously was used to produce PP-randompolymer. The plant comprises a catalyst, alkyl, donor, propylene and ethylene feed systems, loop reactor and a fluidized bed gas phase reactor (GPR). Said components are fed to the loop reactor. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the GPR. The formed polymer and unreacted propylene where separated after removal from the GPR.

The catalyst used was a highly active and stereospecific ZN-catalyst made according to US Patent No. 5,234,879. The catalyst was prepolymerized with propylene (the mass ratio of PP/cat was 10) in batch according to Finnish Patent No. 95387. The prepolymerized catalyst was contacted with triethylaluminium (TEA) and dicyclopentyldimethoxysilane (DCPDMS) (Al/Ti ratio was 135 and Al/Do 10 (mole)) before feeding to the loop reactor.

The catalyst was fed according to US Patent No. 5.385.992 and was flushed with propylene to the loop reactor. The loop reactor was operated at 50 bar pressure, 75 °C temperature and a mean residence time of the catalyst of 1 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer produced in the loop was set at 0 2 via hydrogen feed. The ethylene content was adjusted to 3.5 % w/w via ethylene feed.

The polymer slurry from the loop reactor was transferred to the GPR. The GPR reactor was operated at 29 bar total pressure and 21 bar partial pressure of propylene, 80 °C temperature and mean residence time of the catalyst at 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-random polymer taken out of the GPR was controlled to be 3 via partial pressure of hydrogen. The ethylene content was controlled to be 1.8 % w/w via production split between the reactors. Desired ethylene content was achieved by using a production split of 40 % in loop and 60 % in GPR.

Claims

1. A process for preparing propylene copolymers, which comprises the steps of

   - polymerizing propylene with comonomers in the presence of a catalyst at an elevated temperature of 60 to 85°C and at an elevated pressure in at least one slurry reactor and at least one gas phase reactor, at least 10 % of the polymer product being produced in the gas phase reactor(s),
   - recovering from the slurry reactor a copolymerization product containing unreacted monomers and
   - conducting the copolymerization product to a first gas phase reactor essentially without recycling of the unreacted monomers to the slurry reactor before the gas phase reactor.

2. The process according to claim 1, wherein the polymerization product of the slurry reactor comprises polymeric substances selected from the group consisting of polypropylene, propylene copolymers and mixtures of polypropylene and propylene copolymers.

3. The process according to claim 1 or 2, wherein the comonomer is selected from the group of C_2 to C_{16} olefins.

4. The process according to claim 3, wherein the comonomer is selected from the group of ethylene, 1-butene, 4-methyl-1-pentene, 3-methyl-1-butene, 1-hexene, 1-octene, 1-decene, dienes, vinylcy-

clohexane and cyclopentene.

5. The process according to any of the preceding claims, wherein the slurry reactor comprises a loop reactor and wherein the concentration of propylene and the comonomer in the reaction medium is over 60 wt-% for forming a product in particulate form.

6. The process according to any of claims 1 to 5, wherein the slurry reactor is operated at a temperature in the range of 60 to 75 °C for preparing random and ter-copolymers.

7. The process according to any of claims 1 to 5, wherein the slurry reactor is operated at a temperature in the range of 75 to 85 °C for improved activity and comonomer randomness.

8. The process according to any of claims 1 to 7, wherein less than about 30 % of the unreacted monomers are recycled to the slurry reactor from the gas phase reactor.

9. The process according to any of claims 1 to 8, wherein the slurry reactor is operated at a pressure in the range of 35 to 100 bar.

10. The process according to any of claims 1 to 9, wherein the catalyst is selected from the group consisting of Ziegler-Natta catalysts and metallocene catalysts.

11. The process according to any of the preceding claims, wherein the reaction medium of the polymerization product is evaporated before the polymerization product is fed into a first gas phase reactor.

12. The process according to claim 11, wherein the polymerization product is conducted from the slurry reactor to the first gas phase reactor via a jacketed pipe line heated by steam for providing at least a part of the energy needed for evaporation of the reaction medium.

13. The process according to any of the preceding claims, wherein the polymerization product fed to the first gas phase reactor contains copolymers comprising at least 0.5 wt-%, preferably 2 to 16 wt-% of at least one comonomer.

14. The process according to claim 13, wherein the polymerization product is copolymerized in the first gas phase reactor with additional comonomers to increase the comonomer content.

15. The process according to claim 13, wherein the comonomer content is increased to up to 20 wt-%.

16. The process according to any of claims 1 to 13, wherein polymerization in the first gas phase reactor is carried out without additional monomer feed.

17. The process according to any one of the preceding claims, wherein a polymerization product is recovered from the gas phase reactor.

18. The process according to claim 17, wherein the polymerization product is subjected to copolymerization in the presence of comonomers to provide a first modified polymer with improved softness properties.

19. The process according to claim 18, wherein the copolymerization is carried out in a second gas phase reactor arranged in series with the first gas phase reactor.

20. The process according to claim 19, wherein the second modified polymer is subjected to a least one further copolymerization reaction in at least one further reactor.

21. The process according to any of the preceding claims, wherein at least part of the unreacted monomers are recovered from the second and/or third gas phase reactor and recycled back to the previous gas phase reactor(s).

22. The process according to any of the preceding claims, wherein the unreacted monomers recovered from the first gas phase reactor are recycled back to the gas phase reactor.

23. The process according to any of the preceding claims, wherein a part of the unreacted monomers recovered from a gas phase reactor and recycled back to a slurry reactor.

24. The process according to claim 23, wherein the amount of monomers recycled comprises 1 to 50 wt-% of the amount of monomers in the feed of the slurry reactor.

25. The process according to any of the preceding claims, wherein the production rate of the slurry reactor is 10 to 50 wt-%, preferably less than 50 %, of the total production rate of the slurry and the first gas phase reactor

26. The process according to any of the preceding claims, wherein hydrogen is used in at least one reactor as a molar mass modifier.

27. The process according to any of the preceding claims, wherein the catalyst used is prepolymerized before feeding it into the process.

28. A process for preparing propylene copolymers, which comprises the steps of

- subjecting propylene with comonomers to polymerization in the presence of a catalyst at a temperature in the range of 60 to 85°C and at an elevated pressure in at least one slurry reactor to produce a first copolymerization product comprising a propylene copolymer and unreacted monomers,
- recovering the copolymer and the unreacted monomers,
- feeding the copolymer to at least one gas phase reactor,
- feeding essentially all of the unreacted monomers to said gas phase reactor,
- subjecting the copolymer and the unreacted monomers to polymerization in said gas phase reactor to produce a second copolymerization product containing propylene polymer and gaseous substances, and
- recovering the propylene copolymer, at least 10 % of which is being produced in the gas phase reactor(s).

29. The process according to claim 28, wherein the propylene polymer is fed to a further gas phase reactor for copolymerization.

30. The process according to claim 28 or claim 29, wherein hydrogen is used as molar mass modifier in at least one of the reactors.

31. The process according to any of claims 28 to 30, wherein the polymerization in said gas phase reactor is carried out essentially without additional feed of monomers.

32. An apparatus for preparing propylene copolymers, which comprises

- at least one slurry reactor and at least one gas phase reactor, connected in series to form a cascade,
- a conduit interconnecting at least one slurry reactor with at least one gas phase reactor for conducting essentially all of the unreacted monomers from the slurry reactor to the gas phase reactor, and
- means connected to said slurry reactor for feeding propylene and comonomers directly to the slurry reactor.

33. The apparatus according to claim 32, wherein the conduit comprises a jacketed pipe line provided with means for heating it with steam.

34. A propylene copolymer prepared by a process according to any of claims 1 to 33, comprising 2 to 16 wt-% of at least one comonomer and having a randomness of at least 70 %.

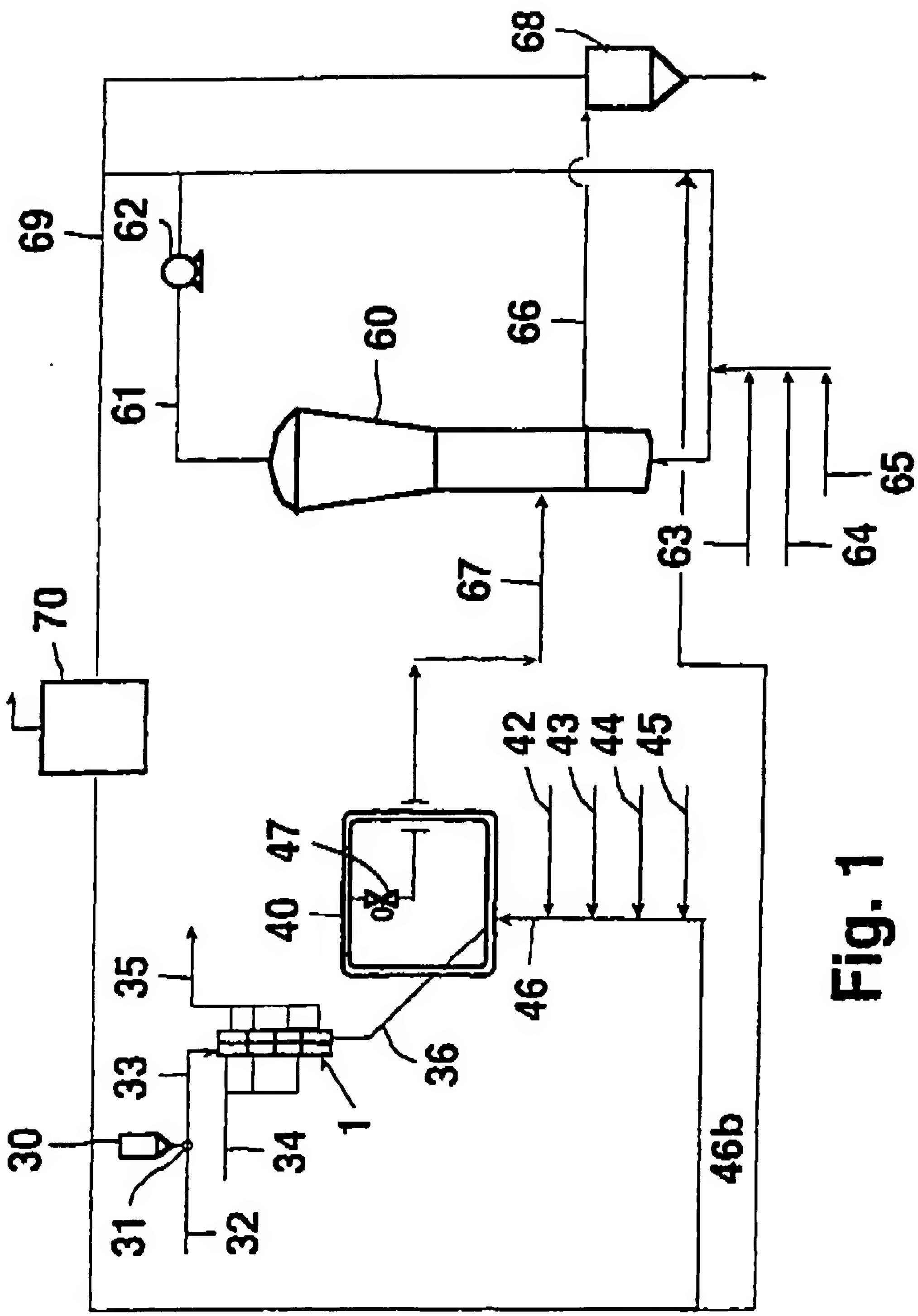

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Fig. 1

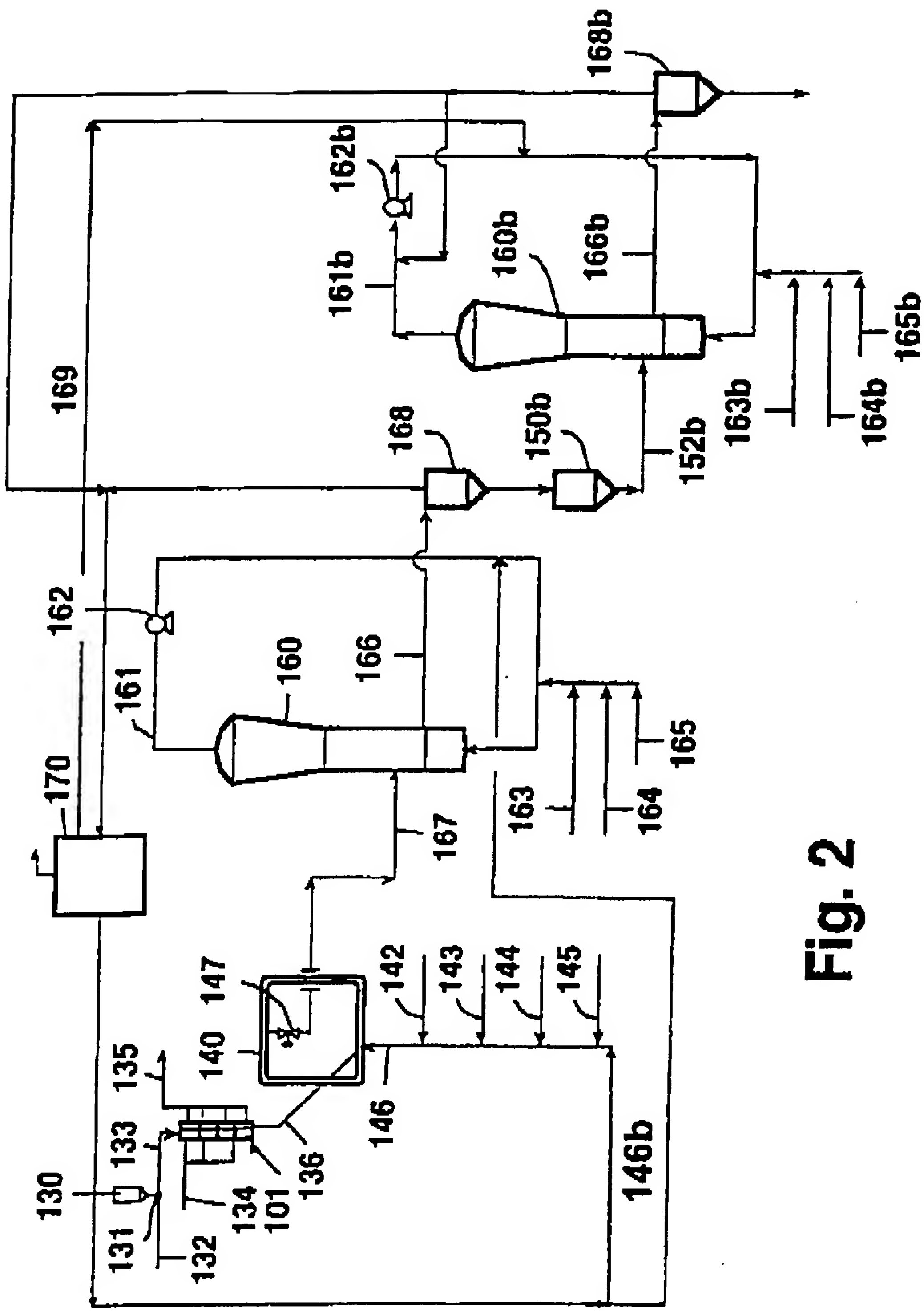
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Fig. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 98 66 0062

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	US 4 740 550 A (FOSTER E GORDON) 26 April 1988 * the whole document * * column 2, line 37 - line 39 * * column 3, line 31 - line 35 * ---	1-11, 13-17, 24-26, 28-34	C08L23/16 C08F10/06 C08F2/00 B01J8/26 B01J19/24
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TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C08F
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 October 1998	Kaumann, E

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EUROPEAN SEARCH REPORT

Application Number
EP 98 66 0062

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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X	WO 96 18662 A (BOREALIS POLYMERS OY) 20 June 1996 * figure * -----	32,33	
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The present search report has been drawn up for all claims

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